

Surface-modified manganese sulfide, method for producing the same and use thereof

5 The invention relates to surface-modified manganese sulfide, a method for its preparation as well as the use of the surface-modified manganese sulfide as an auxiliary press material and as an additive in the sintering of molded articles. Furthermore the present invention relates to a sinter powder containing an amount of the surface-modified manganese sulfide, a method for the preparation of a molded article using the inventive sinter powder as well as a molded article obtainable by the method.

15 The machined processing, especially by cutting, of sintered molded articles is often quite difficult due to tool wear and is alleviated by the addition of sulfides. Manganese sulfide (MnS) has proved to be an especially suitable additive for sintering, since its thermal stability allows it to participate in the sintering process without thermal degradation. For this, the manganese sulfide must be incorporated into the sinter powder in as finely dispersed a form as possible. In the U.S. patent 3,705,020, a manganese sulfide particle size of 10 to 100 μm , preferably 30 to 40 μm is cited and, according to the European patent application EP 25 0 183 666, the particle size is 10 μm or less. A small particle size enables homogeneous incorporation of the sulfide and the production of mechanically stable molded articles. In particular, the crack formation is reduced.

30 However, the small particle size and the large surface of the manganese sulfide associated therewith promotes its reaction with, in particular, moist air to MnO , MnO_2 and MnSO_4 and, with this, a clumping together to larger particles or agglomerates. This behavior causes not only storage problems; 35 in the use of the manganese sulfide as a sinter additive, the clumping then leads to a structural weakening of the finished molded articles. Especially under mechanical and thermal

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stress, the formation of cracks and the destruction of the molded articles follow.

In the U.S. patent 5,768,678, the use of a special composition containing manganese sulfide as a sinter additive is proposed to avoid the oxidation of the manganese sulfide. This composition is made of a mixture of 50-65 wt.% manganese, 30-38 wt.% sulfur and 5-25 wt.% iron and is added to the metal powder to be sintered in an amount 0.2-2.0 wt.%. According to this patent, the oxidation protection is afforded by the iron, which should be present in non-oxidized form. It is, however, a disadvantage of the sinter additive of U.S. 5,768,678 that it contains additional useless iron sulfide and, furthermore, a surface reaction can be merely reduced but not avoided. A further disadvantage of this sinter additive is its costly production.

There therefore exists a need for a storable and easily obtainable manganese sulfide. It is therefore the goal of the present invention to provide such a manganese sulfide without the features known in the prior art.

The inventors have surprisingly found that such a manganese sulfide can be obtained in that powdered manganese sulfide is provided, a coating agent selected from a wax, an ester of an inorganic or organic acid or a polymer with a low melting point or mixtures thereof is selected, is added in an amount of 0.01 to 10 wt.% relative to the weight of the manganese sulfide used, and the mixture is mixed over a period of time which is sufficient to ensure a homogeneous mixture.

The studies of the inventors have indicated that the oxidation protection and the reduction of the moisture uptake by the otherwise hygroscopic material and the agglomeration resulting therefrom are surprisingly prevented by even small amounts of the coating agent.

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According to the invention coating agent is used in the production of the coated manganese sulfide in an amount of 0.01 wt.% to 10 wt.%, preferably 0.01 to 5 wt.%, especially preferred 1.0 to 3.0 wt.% relative to the weight of the manganese sulfide.

Depending on the melting point of the coating agent, the coating is generally carried out at a temperature of 20°C to 150°C. Depending on the coating agent used, one can however also operate at a temperature around the freezing point (0°C). Preferably, one operates around room temperature, since then, the mixer does not have to be heated. The mixing is normally performed for a period of time of 1 minute to 60 minutes, preferably for 5 minutes to 20 minutes.

Surprisingly, the manganese sulfide obtained in this way can be used directly, in other words it does not have to be submitted to further treatment steps such as drying for storage or for its use.

In addition to the use as a sinter additive for improving the processability of molded sinter articles, it was determined within of the scope of the present invention that the inventive surface-modified manganese sulfide also proves to be a lubricating press auxiliary and it can therefore be generally used as an additive for improving compression characteristics. A further advantageous characteristic of the inventive manganese sulfide, which proves to be very favorable in connection with its storage and use, is that it is dustless.

The coating of the manganese sulfide can be performed in any way known to one of ordinary skill in the art. The coating agent can be added to a conventional mixing apparatus such as a ploughshare mixer or a tumbler-mixer all at once or in intervals. It is for example also possible to spray the coating agent into the mixing container. According to the invention, any normal manganese sulfide can be used,

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irrespective of its purity or particle size. If it is necessary, for example for the use as a sinter additive, the manganese sulfide is finely ground prior to coating, so that in general it has an average particle size, in other words a particle diameter, of 1 to 200 μm , preferably of 1 to 10 μm , and especially preferred of about 5 to 10 μm . It is however also possible in this case to use larger particles, as long as these confer sufficient mechanical stability in later sintering of the molded articles.

According the invention, compounds preferred as coating materials are either liquid at room temperature or have a relatively low melting point of under 150°C . In this way, and as indicated above, it is possible to operate without or only with very weak heating of the mixer in the production of the inventive manganese sulfide.

For the use of the inventive manganese sulfide as a sinter additive, the inventive coating agent should furthermore have an evaporation temperature at normal pressure of under 500°C , preferably in the range of about 200 to 300°C and should decompose or evaporate without residue during the heating of the sinter mixture, since in this way the formation of possible contaminations in the sintered molded article is reduced.

Coating materials used according to the invention and possessing the previously cited physical characteristics are preferably low melting polymers, oils including paraffinic oils and silicon oils, waxes, a mono- or multi-functional aliphatic alcohol with 2 to 12 carbon atoms, organic and inorganic esters, in the latter case especially phosphoric acid esters.

One example of what is to be understood by waxes in the sense of the invention are esters of higher straight-chained fatty acids such as palmitic acid, hexacosanoic acid with higher straight-chained, monofunctional alcohols such as palmityl

alcohol, stearyl alcohol or octadec-9-en-1-ol. Another example of what is to be understood as waxes in the sense of the invention are materials which are mostly of natural origin, which contain the fatty acid esters named above partially or predominantly, and which transition without degradation to a melting liquid, low viscous condition above approximately 30°C to 40°C. An example of such waxes are Japan wax, lanolin or beeswax.

Furthermore, synthetic polymers, with waxy characteristics such as the so-called polyolefin waxes also fall under the definition of waxes here. Examples of such synthetic polymers which find application in the present invention are low-molecular polyethylene glycols and polypropylene glycols.

One example of what is to be understood as oils in the present invention are aliphatic oils based on mineral oil such as the paraffinic oils. The aliphatic oils preferably have a chain length of 6 to 20 carbon atoms. The term oil also further encompasses synthetic oils such as the silicon oils such as known to one of ordinary skill in the art as a general term *inter alia* for clear, colorless, hydrophobic liquids with congealing points of about -80 to -40°C from linear polydimethylsiloxanes and polymethylphenylsiloxanes.

Compounds to be understood here as a low-melting polymer are those which consist of macromolecules and which have a melting point of under 150°C and an evaporation temperature of under about 500°C at normal pressure. Preferred representatives of this class of compounds are polyesters, polyamides and polyaliphatic compounds.

According to the invention, esters of inorganic or organic acids can also be used as the coating agent. Preferred inorganic acids are phosphoric acid and sulfuric acid however other acids can also be used according to the invention such as sulfur acids, carbonic acid, Formic acid and lower carbonic acids with 2 to 6 carbon atoms such as for example

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acetic acid are preferably used as organic acids. Aliphatic as well as aromatic alcohols are used as ester alcohols. The aliphatic alcohols preferably have a chain length of 1 to 20 C-atoms. Preferred aromatic alcohols are the phenols. These
5 can have multiple hydroxyl groups or multiple aliphatic substituents with a chain length of preferably one to six C-atoms.

According to the invention, an alcohol which is to be
10 understood as a mono- or multi-functional aliphatic alcohol with 2 to 12 carbon atoms is one which, due to its evaporation and flammability characteristics, is suitable for use in the inventive method.

15 Aromatic compounds such as biphenyl etc. are also suitable as further coating agents, as long as these compounds, as with the other coating agents usable according to the invention, are characterized by a low-soot and residue-free evaporation.

20 A preferred class coating materials used according to the invention are (low-viscosity) esters of the phosphoric acids, in particular with longer chain aliphatic alcohols with chain lengths between 3 and 15 C-atoms, preferably 6 to 13 C-atoms as well as with phenols or other aromatic alcohols with side
25 chains of 1 to 12 C-atoms, preferably 1 to 3 C-atoms such as cresol. These compounds are known to one skilled in the art as softeners. Examples of such compounds are tris-(2-ethylhexyl)-phosphate, tris(2-butoxyethyl)-phosphate, triphenylphosphate or diphenylcresylphosphate.

30 Diphenylcresylphosphate is an especially suitable representative of this class of compounds, since it is nontoxic, liquid at room temperature and has low viscosity, it evaporates at approximately 230°C and burns soot-free. A further advantage of diphenylcresylphosphate is its relative
35 temperature-independent viscosity.

For the use as a sinter additive, the studies of the inventors have shown that a thusly surface-modified manganese

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sulfide improves the machined processing, especially by cutting, of sintered molded articles if the manganese sulfide is incorporated into a sinter powder in the amount of 0.1 wt.% to 1.0 wt.%, preferably from 0.2 to 0.6 wt.%, relative to the weight of the sinter powder.

Accordingly, a further embodiment of the present invention is directed to a sinter powder characterized by an amount of the inventive manganese sulfide.

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For use as an additive in sintering, the manganese sulfide is preferably treated with the inventive coating agents in the manner explained above prior to the addition to the selected metal powder. However it is also possible within the scope of the invention to first mix unmodified manganese sulfide with the metal powder to be sintered and finally to add the coating agent to the sinter mixture.

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A further embodiment of the present invention therefore also relates to a method for producing a molded article using the inventive sinter powder, wherein the method comprises the following steps:

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- a) compression of the sinter powder in a sinter mold having an inner shape corresponding to the end contour of the finished molded article;
- b) heating the green compact to a temperature above the evaporation temperature of the coating agent used in the production of the manganese sulfide and, if necessary, maintaining the green compact at this temperature for a period of time sufficient to ensure complete evaporation of the coating agent;
- c) sintering the green compact from step b);
- d) removing the cooled molded product from the sinter mold.

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A further embodiment therefore encompasses a molded article obtainable by the inventive production/sinter method elaborated above.

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The present invention is to be described by way of one non-limiting example.

Example 1: Preparation of surface-modified manganese sulfide

20 g of liquid diphenylcresylphosphate were added to 2000 g of manganese sulfide with a particle diameter of 4.96 μm (D50) in a Loedige-mixer. The batch was subsequently mixed at 25°C for 20 minutes.

Determination of the resistance to oxidation

The manganese sulfide, which had been treated with 1% diphenylcresylphosphate, obtained in Example 1 was stored with uncoated manganese sulfide of the same particle diameter, that is according to EP 0 183 666 (Example 2) as well as with a manganese sulfide composition to U.S. 5,768,678 (Example 3) in an atmosphere of 75% humidity at room temperature for 6 days. Subsequently the extent of oxidation of the manganese sulfide on the surface to MnO , MnO_2 and MnSO_4 (according to the schematic reactions $\text{MnS} + \text{H}_2\text{O} \Rightarrow \text{MnO}$; MnO_2 ; MnSO_4) was determined for every sample by measurement of the weight increase (Table 1).

Table 1 Weight increase after 6 days

Example	Manganese Sulfide	Particle size D50	Weight increase
		(μm)	(%)
1	Inventive MnS	4.69	0.2
2	Uncoated MnS	4.49	25.8 %
3	MnS with 10% FeS	7.98	11.1

As can be seen in Table 1, the inventive coated manganese sulfide absorbs significantly less moisture than the uncoated material or the manganese sulfide composition of U.S.

5,768,678. In standing with this, the inventive material is still a fine, free-flowing powder lacking agglomerates after 10 weeks, while during this same time the uncoated manganese sulfide changed to a coarse-grained, dark product due to

absorption of moisture and the formation of manganese dioxide.

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